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Ultrafast Intramolecular Energy Transfer in Water

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Abstract. An unexpectedly fast (0.2 ps) intramolecular energy conversion occurring in H_2O molecules has been revealed using frequency-resolved mid-infrared pump-probe spectroscopy in the spectral region of the OH-stretching vibration.

1. Introduction

Liquid water confined on a nanometer scale has recently raised considerable interest and became a central issue for a wide variety of research areas, ranging from materials to life sciences. The physico-chemical properties of water in geometrically restricted environments differ from those of bulk water, as a result of the truncation of the hydrogen bond network. [1-3] Many of these properties cannot be elucidated without a full understanding of the processes in which only an isolated molecule is involved. A thorough investigation of monomeric water molecules in various liquid matrices has been performed by Graener and coworkers [4]. However, due to a limited temporal resolution of ~15 ps, the vibrational energy transfer was approximated to occur on picosecond or tens of picoseconds time scale, i.e. much slower than in bulk water.

In this contribution, we report time and frequency-resolved mid-IR pump-probe experiments on the OH-stretching modes of monomeric water in acetonitrile. The rotational-free and anisotropy signals were calculated from two orthogonally polarized probe scans [5]. The 100 fs time resolution of our pump-probe experiments reveals rather complicated intramolecular dynamics and rapid decay of anisotropy. Our results show that intramolecular processes play a crucial role in the sub ps water dynamics and strongly suggest that these processes could compete with the intermolecular energy transfer and ultrafast coherence loss in bulk water [6].

2. Results and Discussion

The fundamental stretching transitions for monomeric water in acetonitrile can be easily identified in the absorption spectrum (Fig. 1, squares): the symmetric stretch has a central frequency of 3540 cm^{-1} and the asymmetric stretch is centered at 3630 cm^{-1}. During the pumping process, the stretching modes are populated and

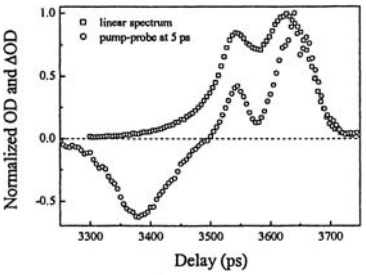

Fig. 1. OH-absorption band (squares) and rotational-free transient spectrum at 0.5 ps delay (circles).

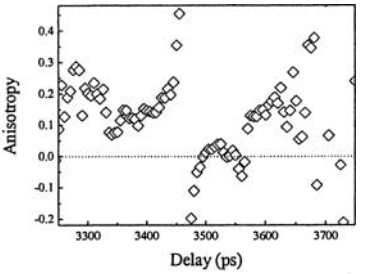

Fig. 2. Anisotropic transient spectrum at 0.5 ps delay

consequently the optical density of the sample changes at all the frequencies corresponding to the transitions in which these levels are involved. The stretching modes population can be monitored by recording the changes in the transmission of a probe pulse following the pumping of the sample. The open circles in Fig. 1 display the transient differential spectrum at 0.5 ps delay between pump and probe. Fig. 2 shows the anisotropy at 0.5 ps delay. A peculiar wavelength dependence can be observed from this graph, with an asymptotic point at 3475 cm^{-1} and a total depolarization around 3525 cm^{-1}.

The rotational-free pump-probe transients show a non-monoexponential behavior (Fig. 3, left panel). For most of the transients, the data at delays longer than 2 ps are well fit by a monoexponential function with 8.3 ± 0.5 ps time constant, which is attributed to the lifetime of the OH stretching mode of a water molecule in acetonitrile [7]. At short delay times, the rotational-free data depend strongly on frequency. For instance, at 3625 cm^{-1}, close to the peak absorption of the asymmetric stretch, the signal decays very fast to about one third of its maximum value (Fig. 3, triangles), while at 3525 cm^{-1}, near the center frequency of the symmetric stretch, the signal slightly increases up to 0.5 ps (Fig. 3, circles). In

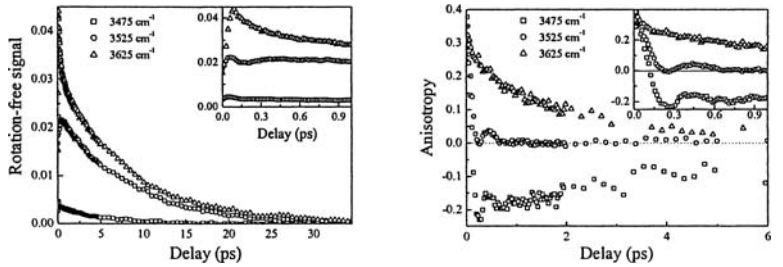

Fig. 3. Rotational-free transients (left) and rotational anisotropies (right) at thee representative wavelengths. The insets show the sub-picosecond evolution of the signals.

both cases, the initial behavior occurs with similar time constants, 0.2 ± 0.05 ps, suggesting an intramolecular energy conversion from asymmetric to symmetric stretching vibration of the H_2O molecule. The evolution between these quantum states, which involves the change of two vibrational quanta, is forbidden in the harmonic potential approximation but becomes possible when the two modes are anharmonically coupled.

The right panel in Figure 3 shows the anisotropy data at several representative wavelengths. The starting value for the anisotropy is close to 0.4, proving that all the relevant processes are resolved. Although the data display a pronounced frequency dependence, two time scales are clearly discernable and most data sets are well described by biexponential functions with times of 0.2 ± 0.1 ps and 2.5 ± 0.5 ps. While the 2.5 ps time clearly reflects the rotational diffusion of the H_2O molecule embedded in acetonitrile matrix [7], the fast component requires further analysis. If we take into account the low concentration of water, which ensures that OH oscillators belonging to different molecules do not interact with each other [6], it becomes clear that an intramolecular process is responsible for the observed memory loss at short times. Again, a change in the quantum state of the vibrating molecule between symmetric and asymmetric modes can explain the experimental data. Thus, the ultrafast energy equilibration between states with quasi-orthogonal orientation of the dipole moments results in a rapid depolarization of the sample. A very peculiar behavior was observed for the anisotropy around 3525 cm^{-1}. In addition to the two characteristic times mentioned above, the signal shows underdamped oscillations with a 450 fs period. These can be explained by the interference between several transitions that contribute to the signal in this spectral region.

In conclusion, our data reveal extremely fast intramolecular processes, which appear to have very similar effects on the spectroscopic observables as the intermolecular interactions observed in bulk water [6]. Therefore, when interpreting experiments in liquid water both intra- and intermolecular processes must be accounted for, especially in the case of nanometer-size droplets, in which their effects are comparable.

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